Nature of magnetic coupling between Mn ions in as-grown Ga$_{1-x}$Mn$_x$As studied by x-ray magnetic circular dichroism

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The magnetic properties of as-grown Ga$_{1-x}$Mn$_x$As have been investigated by the systematic measurements of temperature and magnetic field dependent soft x-ray magnetic circular dichroism (XMCD). The *intrinsic* XMCD intensity at high temperatures obeys the Curie-Weiss law, but residual spin magnetic moment appears already around 100 K, significantly above Curie temperature (T_C), suggesting that short-range ferromagnetic correlations are developed above T_C. The present results also suggest that antiferromagnetic interaction between the substitutional and interstitial Mn (Mn$_{int}$) ions exists and that the amount of the Mn$_{int}$ affects T_C.

Ga$_{1-x}$Mn$_x$As is a prototypical and most well-characterized diluted magnetic semiconductor (DMS) [1]. Because Ga$_{1-x}$Mn$_x$As is grown under thermal non-equilibrium conditions, however, it is difficult to avoid the formation of various kinds of defects and/or disorder. In fact, Rutherford backscattering (RBS) channeling experiments for as-grown Ga$_{0.92}$Mn$_{0.08}$As samples has shown that as many as $\sim$ 17 % of the total Mn ions may occupy the interstitial sites [2]. It is therefore supposed that antiferromagnetic (AF) interaction between the substitutional Mn (Mn$_{sub}$) ions and interstitial Mn (Mn$_{int}$) ions may suppress the magnetic moment [3, 4]. In addition, the random substitution of Mn ions may create inhomogeneous Mn density distribution, which may lead to the development of ferromagnetic domains above Curie temperature (T_C) [5]. The characterization of non-ferromagnetic Mn ions is therefore a clue to identify how they are related with the ferromagnetic ordering and eventually to improve the ferromagnetic properties of Ga$_{1-x}$Mn$_x$As samples. However, it has been difficult to extract the above information through conventional magnetization measurement due to the large diamagnetic response of the substrate and the unavoidable mixture of magnetic impurities.

X-ray magnetic circular dichroism (XMCD), which is an element specific magnetic probe, is a powerful technique to address the above issues. So far, several results of XMCD measurements on Ga$_{1-x}$Mn$_x$As have been reported [6, 7, 8]. From H dependent XMCD studies, the enhancement of XMCD intensity by post-annealing implies AF interaction between the Mn$_{sub}$ and Mn$_{int}$ ions [8]. In the present study, in order to characterize the magnetic behaviors of the Mn$_{sub}$ and Mn$_{int}$,

we have extended the approach and performed systematic temperature (T) and magnetic field (H) dependent XMCD studies in the Mn $L_{2,3}$ absorption edge region of Ga$_{1-x}$Mn$_x$As. We have found that short-range ferromagnetic correlations develop significantly above T_C and that AF interaction between the Mn$_{sub}$ and Mn$_{int}$ is important to understand the magnetic properties of Ga$_{1-x}$Mn$_x$As.

We prepared two as-grown samples with different Mn concentrations; x = 0.042 and 0.078, whose T_C was $\sim$ 60 and 40 K, respectively, as determined by an Arrott plot of the anomalous Hall effect. To avoid surface oxidation, the sample had been covered immediately after the growth of Ga$_{1-x}$Mn$_x$As films by cap layers without exposure to air [As cap/GaAs cap (1nm)/ Ga$_{1-x}$Mn$_x$As(20nm)/GaAs(001)]. The X-ray absorption spectroscopy (XAS) and XMCD measurements were performed at the helical undulator beam line BL23SU of SPring-8 [9]. The XAS spectra were obtained by the total-electron yield mode. The measurements were done without a surface treatment and H was applied to the sample perpendicular to the film surface.

Figures 1 (a) and 1 (b) show the XAS spectra (μ^+ and μ^-) in the photon energy region of the Mn L_3 absorption edge and the corresponding XMCD spectra, defined as $\mu^+ - \mu^-$, at T = 20 K and H =0.5 T for x = 0.042 and 0.078. Here, μ^+ (μ^-) refers to the absorption coefficient for the photon helicity parallel (anti-parallel) to the Mn $3d$ majority spin direction. The XAS spectra for both Mn concentrations have five structures labeled as a, b, c, d and e. The average XAS spectra [defined by $(\mu^+ + \mu^-)/2$] have been normalized to 1 at structure b. The intensity ratio c/b is very different between
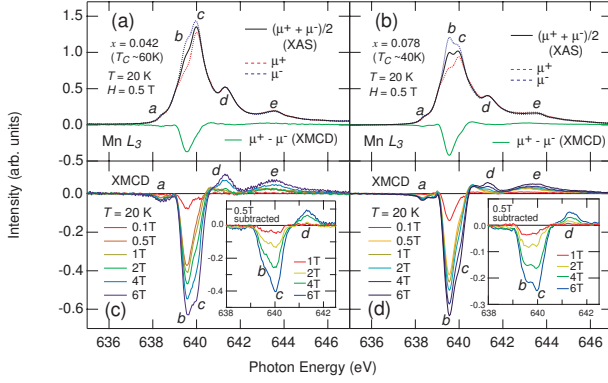
FIG. 1: (Color online) Mn L_3-edge XAS (μ^+, μ^- and (μ^+ + μ^-)/2) and XMCD (μ^+ - μ^-) spectra of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ taken at $T = 20$ K and $H = 0.5$ T for $x = 0.042$ (a) and $x = 0.078$ (b). Panels (c) and (d) show the H dependence of the XMCD spectra for $x = 0.042$ and $x = 0.078$, respectively. Inset shows the difference XMCD spectra obtained by subtracting the XMCD spectrum at $H = 0.5$ T.

$x = 0.042$ and 0.078, indicating that the spectra consist of two overlapping components. Figures 1 (c) and 1 (d) show the H dependence of the XMCD spectra. As H increases, XMCD structures corresponding to structures c, d and e are enhanced, particularly, strongly for the $x = 0.042$ sample. One can see this behavior more clearly in the difference XMCD spectra obtained by subtracting the XMCD spectrum at 0.5 T from the spectra at $H = 1, 2, 4$ and 6 T as shown in the inset of Fig.1 (c) and (d). Recent XAS and XMCD studies have revealed that these structures (c, d, e) are ascribed to contamination of out-diffused Mn ions on the surface [7, 10, 11]. The difference in the XAS intensity ratio c/b is therefore naturally ascribed to the difference in the amount of Mn ions diffused into the cap layer or the surface region during the growth of GaAs on $\text{Ga}_{1-x}\text{Mn}_x\text{As}$. In the following, therefore, we shall neglect those extrinsic signals and focus only on intrinsic signals, particularly structure b, to investigate the intrinsic magnetic behavior.

In order to extract the *intrinsic* XAS spectrum, we assumed that structure b could be ascribed to the intrinsic Mn ions as mentioned above. Therefore, we first obtained the *extrinsic* XAS spectrum as (XAS $x = 0.042$)$-p\times$(XAS $x = 0.078$), where p was chosen so that structure b vanished. The *intrinsic* XAS spectrum was then obtained as (*raw* XAS)$-q\times$(*extrinsic* XAS), where q was determined so that the line shape of the *intrinsic* XAS spectrum agreed with that obtained from the fluorescence yield measurements [10, 11]. Next, in order to extract the *intrinsic* XMCD spectra, we first obtained the *extrinsic* XMCD spectrum as (XMCD at 6 T)$-\alpha\times$(XMCD at 0.5 T), where α was chosen so that an XMCD structure corresponding to structure b vanished by utilizing the fact that the ferromagnetic signals and hence the intrinsic signals should be domi-
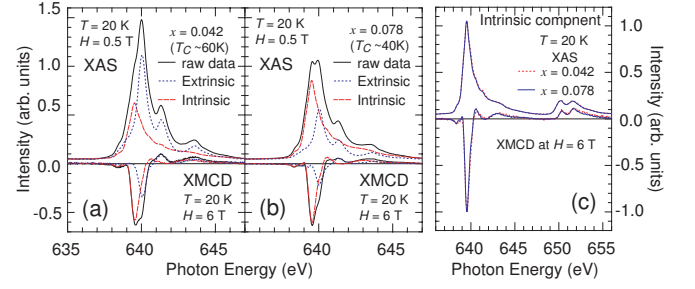

FIG. 2: (Color online) Decomposition of the XAS and XMCD spectra of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ into the intrinsic and extrinsic components for $x = 0.042$ (a) and for $x = 0.078$ (b) in the Mn L_3 edge region. Panel (c) shows comparison of the line shapes of the *intrinsic* XAS and XMCD spectra between $x = 0.042$ and 0.078, normalized to the peak heights.

nant in the XMCD spectrum at low H. The *intrinsic* XMCD spectrum was then obtained as (XMCD at each H)$-\beta\times$(*extrinsic* XMCD spectrum), where β was chosen so that structure c vanished. Figures 2 (a) and 2 (b) show the results of the decomposition of the XAS and XMCD spectra into the intrinsic and extrinsic components for $x = 0.042$ and 0.078, respectively. While the XMCD intensity is enhanced as H increases and T decreases, the line shapes of the *intrinsic* XMCD spectra are unchanged with H and T. The line shapes of the *intrinsic* XAS and XMCD spectra for both Mn concentrations thus agree with each other as shown in Fig. 2 (c), indicating that the decomposition procedure was valid.

Using the *intrinsic* XAS and XMCD spectra, we have applied the XMCD sum rules [12, 13], assuming the Mn $3d$ electron number $N_d = 5.1$ [8], and estimated the spin magnetic moment (M_S) at $T = 20$ K and $H = 0.5$ T to be M_S=2.5±0.2 and 1.7±0.2 (μ_B per Mn) for $x = 0.042$ and 0.078, respectively. These M_S values are much larger than those obtained in the early studies on oxidized surfaces [6] and comparable to the recent ones on etched surfaces [8], indicating that the cap layer protected the ferromagnetic properties of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$. The ratio M_L/M_S is estimated to be 0.07 for both concentrations, where M_L is the value of the orbital magnetic moment, showing that the intrinsic Mn ion has a finite, although small, M_L, probably because of certain deviation from the pure Mn^{2+} (d^5) state.

The T dependence of M_S from the XMCD signal for $H = 6$ T is plotted in Fig. 3 (a). As T decreases, the XMCD signal is increased monotonously except for the discontinuity at around T_C (~ 60 K for $x = 0.042$, ~ 40 K for $x = 0.078$). This discontinuity probably reflects the ferromagnetic ordering which aligns the magnetization parallel to the sample surface, the easy axis of magnetization in the films [14]. It should be noted that M_S increases monotonously even well below T_C as T decreases, indicating that full spin polarization is not achieved even well below T_C. For $x = 0.078$, the T dependence for $H =$
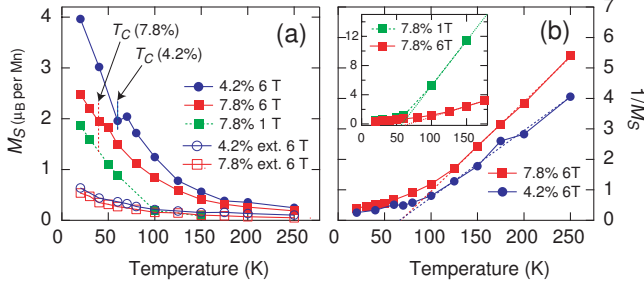
FIG. 3: (Color online) T dependence of the spin magnetic moment M_S. (a) T dependence of M_S for $H = 6$ T. For $x = 0.078$, results for $H = 1$ T are also plotted. Open symbols show that of the extrinsic component at $H = 6$ T. (b) T dependence of the inverse of M_S. Inset shows comparison between 1 and 6 T for $x = 0.078$.

1 T shows essentially the same behavior as that for 6 T. Figure 3 (b) shows the inverse of M_S plotted in Fig 3 (a). The high-temperature part is well described by the Curie-Weiss (CW) law, independent of H as shown in the inset of Fig. 3 (b).

Figure 4 shows the H dependence of M_S at several temperatures for $x = 0.042$ [panel (a)] and 0.078 [panel (b)]. M_S of the intrinsic component is increased rapidly from $H = 0.1$ to 0.5 T, due to the re-orientation of the ferromagnetic moment from the in-plane to out-of-plane directions [14]. Above 0.5 T, M_S is increased almost linearly as a function of H. We have plotted the T dependence of $M_S|_{H\to0\mathrm{T}}$ obtained from the linear extrapolation of M_S at high fields to $H = 0$ T and $\partial M_S/\partial H|_{H>0.5\mathrm{T}}$ (μ_B/T per Mn) (the susceptibility of the paramagnetic component) in Fig. 4 (c) and (d), respectively. For the extrinsic component, $M_S|_{H\to0\mathrm{T}}$ is vanishingly small at all temperatures and $\partial M_S/\partial H|_{H>0.5\mathrm{T}}$ is increased as T decreases following the CW law, indicating that the extrinsic component is paramagnetic and decoupled from the ferromagnetism of the intrinsic component. As for the ferromagnetic component, $M_S|_{H\to0\mathrm{T}}$ is steeply increased below ~ 100 K. i.e., from somewhat above T_C. The T dependence of $M_S|_{H\to0\mathrm{T}}$ [Fig. 4 (c)] is correlated with the deviation from the CW law below ~ 100 K [Fig. 3 (b)]. Well below T_C, $M_S|_{H\to0\mathrm{T}}$ still continues to increase with decreasing T, indicating the inhomogeneous nature of the ferromagnetism. As for $\partial M_S/\partial H|_{H>0.5\mathrm{T}}$, unlike the extrinsic component, it saturates around T_C and is not increased as T further decreases. The appearance and increase of $M_S|_{H\to0\mathrm{T}}$ between T_C and ~100 K [Fig. 4 (c)] strongly suggest that short-range ferromagnetic correlations start to develop and ferromagnetic domains form before the long-range order is established at *macroscopic* T_C. Each ferromagnetic domain may have different ferromagnetic behavior due to the spatial distribution of T_C in the as-grown samples. Those results may correspond to the theoretical prediction that ferromagnetic domains
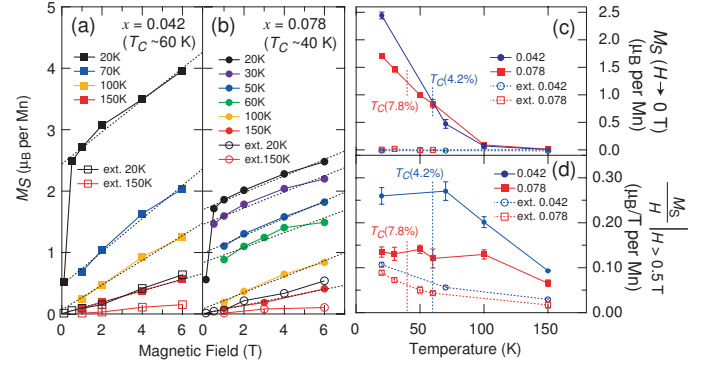

FIG. 4: (Color online) H dependence of M_S for $x = 0.042$ (a) and for $x = 0.078$ (b) at several temperatures. Dashed lines show fitted straight lines above 0.5 T. (c) T dependence of the residual magnetization $M_S|_{H\to0\mathrm{T}}$ (M_S for $H \to 0$ T). Open symbols show that of the extrinsic component. (d) T dependence of the slope of the M_S-H curve above 0.5 T, i.e., the high-field magnetic susceptibility ($\partial M_S/\partial H|_{H>0.5\mathrm{T}}$). Open symbols show that of the extrinsic component.

develop above T_C when there is magnetic inhomogeneity [5].

The suppression of the CW-like increase of $\partial M_S/\partial H|_{H>0.5\mathrm{T}}$ below T_C in both samples indicates that AF interaction between the ferromagnetic Mn i.e., Mn_{sub} and non-ferromagnetic (or paramagnetic) Mn such as Mn_{int}. The recent H dependent XMCD study of $\mathrm{Ga}_{1-x}\mathrm{Mn}_x\mathrm{As}$ shows that $\partial M_S/\partial H|_{H>0.5\mathrm{T}}$ becomes small and $M_S|_{H\to0\mathrm{T}}$ becomes large after post-annealing, suggesting that the changes are caused by a reduction of Mn_{int} [8]. In the present study, $\partial M_S/\partial H|_{H>0.5\mathrm{T}}$ and $M_S|_{H\to0\mathrm{T}}$ are smaller for $x = 0.078$ than for $x = 0.042$ [Fig. 4 (c) and (d)], suggesting that AF interaction becomes stronger for $x = 0.078$ than that for $x = 0.042$. This is reasonable because the number of Mn_{int} is expected to be larger for larger Mn concentration. Assuming that M_S per the Mn_{sub} is 5 (μ_B per Mn) and M_S of the Mn_{int} is antiparalleled to that of Mn_{sub}, the ratio of Mn_{int} atoms in the intrinsic component (R_{int}) is estimated as 0.26 for $x = 0.042$ and 0.33 for $x = 0.078$ from $M_S|_{H\to0\mathrm{T}}$ at 20 K. This is consistent with the result of the RBS experiment [2], which R_{int} is estimated as 0.17 for an as-grown sample with T_C= 67 K, indicating that T_C is strongly correlated with the amount of Mn_{int}. We have fitted the susceptibility $\partial M_S/\partial H|_{H=6\mathrm{T}}$ (μ_B/T per Mn) of the intrinsic component above 100 K [Fig. 3 (b)] to the CW law with an offset, $\partial M_S/\partial H|_{H=6\mathrm{T}} = N_xC/(T - \Theta) + \partial M_S/\partial H|_0$, where $C = (g\mu_B)^2S(S+1)/3k_B$ is the Curie constant, Θ is the Weiss temperature, $\partial M_S/\partial H|_0$ is the constant offset, N_x is the number of magnetic Mn ions in the sample with Mn concentration x, and g is the g factor. Θ is estimated to be 68±5 K for $x = 0.042$ and 69±3 K for $x = 0.078$. $\partial M_S/\partial H|_0$ is estimated to be of order of

$\sim 10^{-3}$ for both samples. Assuming $g = 2$, $S = 5/2$ and $\Theta = 68$ K, one obtains $N_{0.042} = 0.97$ and $N_{0.078} = 0.67$. This result strongly suggests that most of the intrinsic Mn ions in the $x = 0.042$ sample participate in the paramagnetism above ~ 100 K and the paramagnetism in the $x = 0.078$ sample is suppressed even at high temperatures, again implying that the AF interaction is stronger and more influential in the $x = 0.078$ sample.

In conclusion, we have investigated the T, H and Mn concentration dependences of the ferromagnetism in as-grown $Ga_{1-x}Mn_xAs$ samples by XMCD measurements to extract the intrinsic magnetic component. The XMCD intensity deviates from the CW law below ~ 100 K, indicating that the ferromagnetic moment starts to form at ~ 100K and that the short-range ferromagnetic correlations develop significantly above T_C. The high-field magnetic susceptibility becomes T-independent below T_C, indicating that the AF interaction between the Mn_{sub} and Mn_{int} ions, which becomes strong as the Mn concentration x increases, plays an important role to determine the magnetic behavior of $Ga_{1-x}Mn_xAs$. In addition, the amount of the Mn_{int} ions should be strongly related with T_C. The present experimental findings should give valuable insight into the inhomogeneous magnetic properties of many DMS's. In future studies, it is very important to perform a detail T and H dependent XMCD study for a post-annealed samples.

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